THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

AUGUST 1925.

XXXIII. *The Photoelectric Effect in Potassium Vapour as a Function of the Frequency of the Light.* By Ernest Orlando Lawrence*, *M.A., Sloane Fellow in Physics, Yale University*†.

Introduction.

BECAUSE of our ignorance of the precise nature of the ejection of electrons by light from solid surfaces, that is to say, because of the complexities involved in the photoelectric mechanism for solids which the Bohr theory has not yet encompassed, experimental facts of this sort do not bear vitally on the Bohr conceptions. On the other hand, experimental data on the photoelectric effect in vapours have a direct significance in the Bohr theory, inasmuch as in this instance the atoms are isolated and free to act the *rôle* to which the theory applies. Information of the latter sort is meagre. Steubing ‡ has described an experiment which seemed to show ionization in mercury vapour by light transmitted through fused quartz. Anderson § and Gilbreath ‖ have obtained ionization in potassium vapour which they attribute to a photoelectric effect in the vapour, but which probably resulted from a photoelectric effect from the electrodes. Kunz and Williams ¶ have observed

* A dissertation presented for the degree of Doctor of Philosophy at Yale University.

† Communicated by Professor W. F. G. Swann.

‡ *Phys. Zeit.* x. p. 787 (1909).

§ Phys. Rev. i. p. 233 (1913).

‖ Phys. Rev. x. p. 166 (1917).

¶ Phys. Rev. xv. p. 550 (1920); xxii. p. 456 (1923).

a photoelectric effect in cæsium vapour having a threshold coincident with the limiting frequency of the principal series of the vapour, and Williamson * has indicated that the threshold for potassium vapour lies between 2800 Å. and 3100 Å., and has also shown that the efficiency of the light in producing the effect increases rapidly with the frequency. The present paper is an account of an experimental investigation of a more quantitative nature of the photoelectric effect in potassium vapour.

Experimental Arrangements.

The investigation of the photoelectric effect in vapours involves fundamental experimental difficulties, some of which are augmented when potassium vapour is used. It is well known that potassium is exceedingly active photoelectrically and thermionically, and the difficulties in differentiating a true photoelectric effect in the vapour from thermionic currents and photoelectric currents from the electrodes and other portions of the chamber are obvious. Various experimental methods were tried, culminating in the adoption of a method similar to that which Williamson used in his investigation. It became clear that the electrodes involved in measuring the ionization had to be kept at a temperature low relative to the temperature of the vapour requisite to produce sufficient vapour density. To meet this condition a jet of potassium was caused to traverse a chamber and condense on a liquid-air-cooled surface. The ions produced by light passing through the jet of vapour were collected by an arrangement of electrodes in a cool portion of the chamber. A collimating and diaphragming system caused the light to traverse the jet without impinging on metal parts of the chamber, thereby reducing to a minimum spurious photoelectric effects. In this way thermionic effects were reduced to a negligible order of magnitude, and restricted photoelectric effects from the electrodes and other portions of the chamber practically to effects arising from light scattered by the vapour.

The experiment was primarily a determination of the magnitude of the photoelectric ionization in the vapour per unit intensity of light as a function of the frequency. Hence a source of monochromatic light sufficiently intense to produce measurable photoelectric effects, and a means of measuring the light of intensity simultaneously with the observation of the effect in the vapour, were essentials.

* Phys. Rev. xxi. p. 107 (1923).

Preliminary experiments showed that quartz-mercury lamps were totally inadequate sources of illumination, and that light from a Pfund iron arc resolved into bands of from forty to eighty ångströms produced measurable ionization in the potassium vapour. It perhaps is of interest to note in this connexion that the photoelectric effects in the vapour produced by these relatively small bands of wave-lengths from the iron arc were as large as the effects obtained from the whole spectrum of a quartz mercury lamp. The intensity of the light was measured by a potassium photoelectric cell which in turn was calibrated by a thermopile and galvanometer.

Figs. 1 and 1 *b* show diagrammatically the arrangement of the apparatus. Distilled potassium K in the reservoir R

Fig. 1.

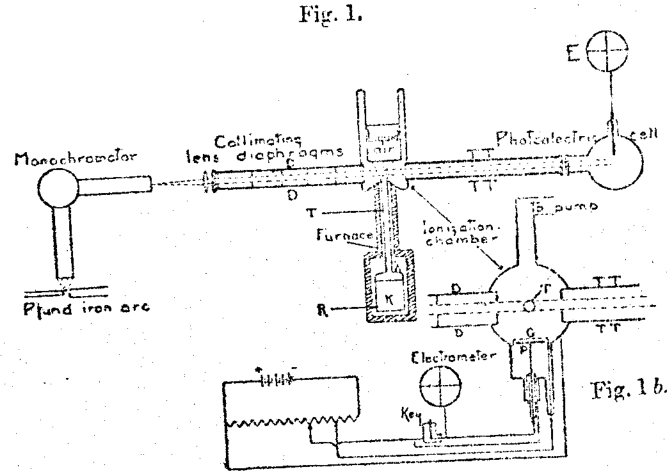


Fig. 1 *b*.

was heated by a furnace, causing a jet of vapour to issue up through a tube T (20 cm. in length) into the ionization chamber and on to a liquid-air-cooled surface, as the dotted lines indicate. Of course the jet was in no sense of the word unidirectional, and a good portion of the vapour entering the chamber condensed on portions of the chamber other than the liquid-air flask. Dotted lines also indicate the course of the light which, originating in the Pfund arc, passed into a monochromator. The band of wave-lengths from the monochromator after collimation by a quartz lens passed through a quartz window into a tube D (50 cm. long) containing a series of diaphragms. From the diaphragms the light passed into the ionization chamber, traversing the stream of vapour and out through a diaphragm into a second tube TT, and finally out through a quartz window into an adjacent photoelectric cell. The last diaphragm of the series in tube D was larger than the others, so that sensibly none of the light in the beam impinged on it. This last diaphragm cut off from the ionization chamber diffusely scattered light in the tube D, which was due to reflexions of the beam from the edges of the adjacent diaphragms. The single diaphragm in tube TT also was larger than the cross-section of the light beam, so that no portion of the beam suffered reflexion back into the chamber before entering the tube. The diagram does not properly indicate the orientation of the quartz window at the end of TT, as it was mounted so that the normals of its surfaces were at an angle with the direction of the beam of light passing through. This caused reflected light to strike the walls of the tube and to experience many reflexions before re-entering the ionization chamber. Both the interior of the tubes and the diaphragms of D and T were black. This optical system accomplished the purpose of preventing light from the monochromator striking any portion of the chamber appreciably (visible light passed through the chamber in this manner produced no discernible illumination therein). As has been mentioned before, this rather elaborate system of collimation of the beam was necessary, as without it stray light falling on the electrodes produced large spurious effects. This fact revealed itself early in the preliminary experiments.

The photoelectric cell placed at the exit end of TT to measure the intensity of the light passing through the vapour was of the Hughes * type, consisting of a flask coated on the interior with pure potassium metal. Light entering the cell through a quartz window experienced many reflexions on the potassium surface, thereby producing relatively large photoelectric currents in the cell. The sensitivity of the cell could have been further increased in the well-known manner by the introduction of suitable gases, but it was desired to have the potassium surfaces as free from contamination as possible, in order that existing data on the photoelectric selectivity of potassium could be made use of in a qualitative way. The diagram indicates an electrometer E attached to the cell. The electrometer measured the currents in some instances by the simple rate of deflexion method, and at other times the electrometer measured the fall in potential which the photo currents

* Hughes, Phil. Mag. xxv. p. 679 (1913).

produced in passing through india ink resistance of the order of magnitude of 10^{10} ohms. The india ink resistance method ultimately was used entirely, as it was found in every respect more desirable.

The furnace surrounding the reservoir and jet tube was of brass tubing wound with resistance coils embedded in alundum cement, and was insulated thermally by asbestos. It possessed sufficient "heat inertia" to ensure that temperature changes were slow.

Fig. 1 *b* is a horizontal section of the ionization chamber depicting the electrode arrangement. The circle in the centre D represents the jet, and the dotted lines indicate the course of the light in its passage through the chamber across the vapour. The electrodes G, P are in a cool portion of the chamber at the side of the vapour jet. Because of the abundance of stray electrons of thermionic origin always present, the positive ions formed in the jet by the light were measured. An accelerating potential (relative to the positive ions) between the walls of the chamber and a grid G drew the positive ions to the grid, where a good share passed through and after traversing a smaller retarding field impinged on a plate P. An attached electrometer system deflected this positive ion current on to the plate. As was the case for the photoelectric cell currents, in this instance also both the rate of deflexion method and the high resistance method were used, culminating in the adoption in the final experiments of the latter. For simplicity the diagram indicates the arrangement for measuring the positive ions by the rate of deflexion of the electrometer. The modification involved in using the resistance method is perfectly obvious. For the rate of deflexion method an electrometer sensitivity was used of 800 mm. per volt, while for the resistance method the Dolezalek electrometer had a sensitivity of 6000 mm. per volt at a scale distance of 1·6 m. and was critically damped. The resistances used were of the order of $5\times10^{1?}$ ohms, and were made of fine ruled lines of india ink on paper hermetically sealed in glass tubes.

Constructional details of the apparatus hardly merit further description. Suffice to say that the ionization chamber and the tubes D and TT with diaphragms were of brass, and the jet and reservoir and the liquid-air flask were of pyrex glass and were attached to the brass ionization chamber by wax joints. Because of the high temperature of the jet an air blast played over the wax joint, keeping it properly cooled.

Mercury diffusion pumps in conjunction with a liquid-air trap and McLeod gauge comprised the vacuum system.

Experimental Procedure.

The ionization chamber (and appending parts) was exhausted by the pump system to pressures which registered on a McLeod gauge less than 10^{-5} mm. of mercury. This vacuum was maintained during the course of a day, during which time potassium metal was distilled into the boiler. From the time of distillation of the metal to the completion of an experimental run the pumps were kept on the apparatus, thereby continually removing gases evolved from the metal and other portions of the chamber. After the completion of the distillation of the potassium into the apparatus immediately the iron arc and monochromator were adjusted so that light of maximum intensity passed through the chamber. Clearly this was obtained by an adjustment for a maximum current from the photocell. The furnaces were then turned on and brought to a fairly constant temperature in the neighbourhood of 300° C., and with suitable potentials on the electrodes the apparatus was ready for the observation of the photoelectric effects.

Preliminary experiments had shown that light of wave-length greater than 3000 ångströms apparently produced no appreciable photoelectric effects in the vapour, so that wave-lengths only of this order or shorter were used in the final experiments. It was found that a fairly intense band of wave-lengths emerged from the monochromator set at 2560 angströms (with slit-widths of 1 mm.), which produced a very readily measurable effect in the ionization chamber. The monochromator was set at this adjustment at the beginning of a run, and when conditions became steady, that is to say when both photo currents were observed to be quite constant, their magnitudes were taken down, and immediately the monochromator was adjusted to a new wave-length setting and the new values for the photo currents were noted. Next an observation with the former setting was made as a check on any change in conditions between observations. Clearly this procedure of taking observations in groups of three wherein the first and third were for the same wave-length permitted a close check on the variation of such things as the vapour density in the jet. This method of observation was extended over the whole range of useful wave-lengths, that is to say from 2200 ångströms on up. Inasmuch as the vapour rapidly distilled out of the boiler, it was necessary to work as quickly as possible. Observations were taken at the rate of about one per minute, a greater speed being prohibited by the natural period and damping of the deflexions of the electrometer needles. However, inasmuch as a run lasted over two hours, it was possible to get a fair number of readings over the whole range of investigation. Perhaps it should be mentioned in this connexion that with advancing time the level of the molten potassium in the reservoir lowered, and in order to maintain the same vapour density in the jet the temperature of the furnaces was gradually raised to compensate the effect of the change in position. The approach of the complete disappearance of the potassium from the reservoir evidenced itself very markedly by a lowering of the vapour-pressure in the jet and consequent ultimate disappearance of the photoelectric currents in the ionization chamber.

As has been mentioned above, the photoelectric currents were measured either by the rate of deflexion of the electrometer needles, that is by the deflexion during a definite period of time, or by the fall in potential produced by the currents flowing through high resistances of india ink. The latter case involves simply noting the deflexion of the electrometer when things are in equilibrium, while the rate of deflexion method is liable to error unless certain considerations are recognized. If the observed deflexions are to be proportional to the currents, Professor Swann * has pointed out that the deflexions must be taken over periods of time which are multiples of the natural period of oscillation of the electrometer needle. A subsidiary requirement also is that the period of observation must not extend from the time of opening the electrometer key, but from a short time later—of the order of one or two seconds. With this in mind, the two methods gave consistent values for the observed currents.

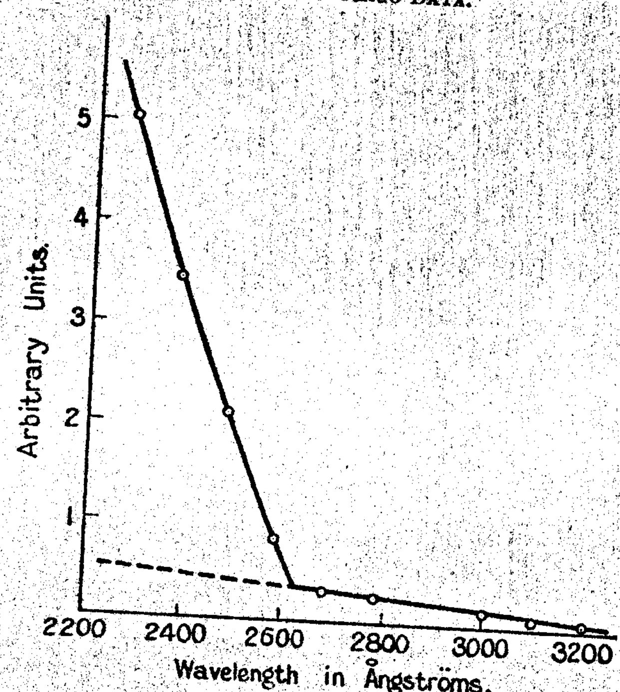
Results.

This experimental investigation was begun at the University of Chicago during the last academic year, and has been continued during the present year at Yale University. In view of the differences in the experimental apparatus at both places, it is desirable to present the results separately. As will be indicated below, the results of last year's work seemingly are at variance with what would be expected from

* Swann, Phil. Mag. xxiv. p. 445 (1912).

the Bohr standpoint, and the results of the present year form a rather significant check on the preceding year's work.

Fig. 2.—"Chicago Data."



Ordinates are ratios (arbitrary constant):—

$$\frac{\text{Photoelectric effect in potassium vapour.}}{\text{Photoelectric effect in potassium photocell.}}$$

Abscissæ are:—

Mean wave-length of band of wave-lengths producing photoelectric effects simultaneously in vapour and in photocell.

Both photoelectric currents measured by rate of deflexion method with electrodes at following potentials:—

Walls of ionization chamber	0·0 volts.
Grid	−12·0 „
Plate	−10·8 „

The curve of fig. 2 embodies the results obtained last year at Chicago. This typical curve is for a single experimental run—that is to say, it represents the data obtained during the time that a single reservoir full of potassium distilled into the ionization chamber. The points of the curve are the averages of the observations during the run corrected

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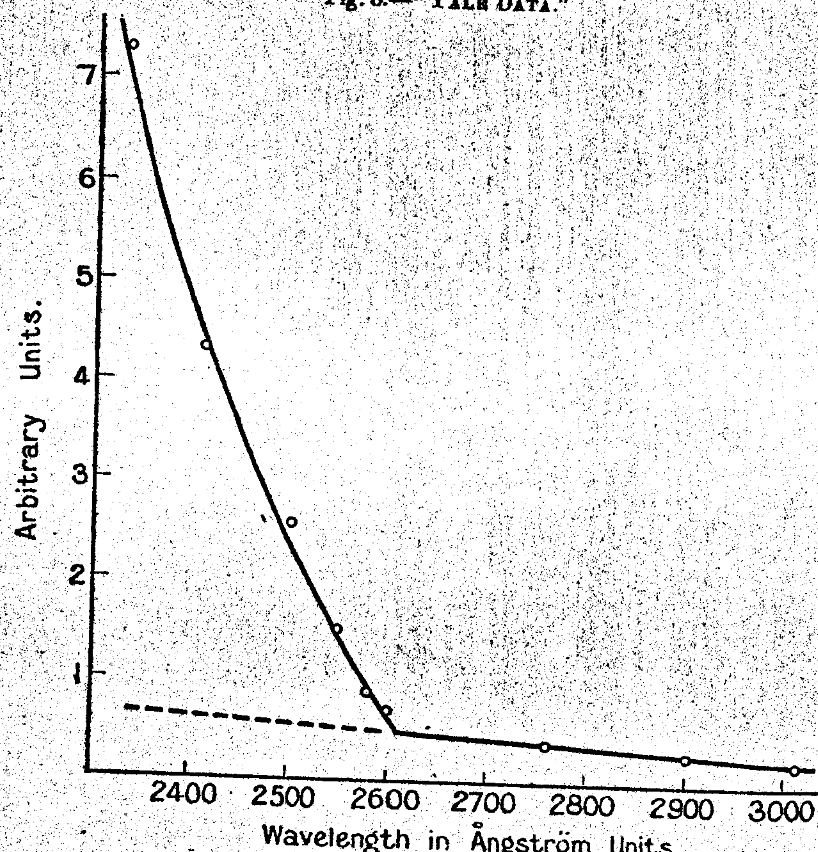
for changes in the density of the vapour-stream, as indicated in a paragraph of the experimental procedure. The ordinates are the ratios (times an arbitrary constant) of the photo-electric currents from the vapour to the photo currents from the photocell, produced by bands of wave-lengths emerging from the monochromator when adjusted at a wave-length setting given by the abscissæ. It is clear that if the photocell were equally sensitive to all wave-lengths, and the light emerging from the monochromator were monochromatic, the curve would represent the variation of the photoelectric effect in the vapour per unit light intensity with the frequency. Neither of these conditions subsisted in the experiment, so that the curve representing the variation per unit intensity with the frequency has a somewhat different form.

A Hilger monochromatic illuminator was used at Chicago, and the data of the above curve were obtained with slit-widths of 1·2 mm. A spectroscopic examination of the quality of the light emerging from the monochromator revealed that roughly 90 per cent. of the light was contained in bands of from fifty to a hundred ångströms (depending on the wave-length setting), which were symmetrical with respect to the wave-length for which the monochromator was adjusted. The remaining portion of the light was distributed throughout the spectral range, and of especial significance was the fact that there was always transmitted some light of much shorter wave-lengths. With this information it is possible to get at the significance of the curves.

The curve is represented quite closely by two intersecting straight lines, and is linear over intervals about the experimentally given points through which the curve is contructed. This point of intersection strikingly suggests itself as the photoelectric threshold for the vapour—that is, the abscissa of this point is the longest wave-length able to produce a photoelectric effect in the vapour. The photoelectric effects observed for wave-lengths greater than this threshold value represented by the portion of the curve to the right of the intersection are attributed to stray light of shorter wave-lengths transmitted by the monochromator, and to a small photoelectric effect from the electrodes due to a small amount of scattered light.

Now let us consider the experimental points making up the portion of the curve to the left of the threshold. The photoelectric effects here arise from both stray effective wave-lengths and the bands of wave-lengths symmetrically placed about the values given by the abscissæ. Because of the linearity of the curve over these bands, it is clear that the assigned abscissæ are approximately the effective mean values for the wave-lengths of the bands, and allowing for the stray light, this portion of the curve represents the variation of the ratio of the photoelectric effect in the vapour to the effect in the photocell with the wave-length.

Fig. 3.—"Yale Data."



Ordinates and abscissæ same as Fig. 2.

Photoelectric currents measured by high-resistance method with electrodes at the following potentials.

Walls of ionization chamber	0·0 volts.	
Grid	−22·0	„
Plate	−19·8	„

The amount of spurious effect in this region has not been determined, but probably is not far from that obtained by

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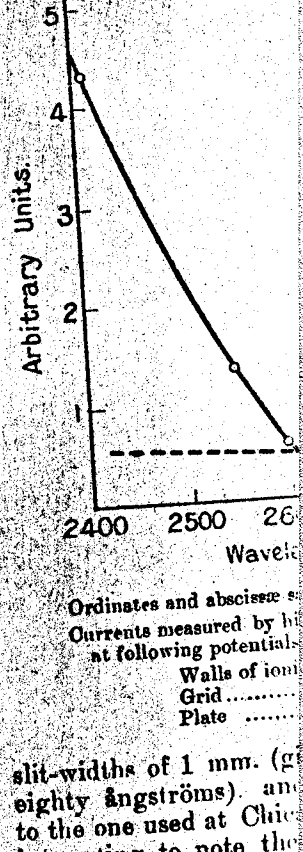

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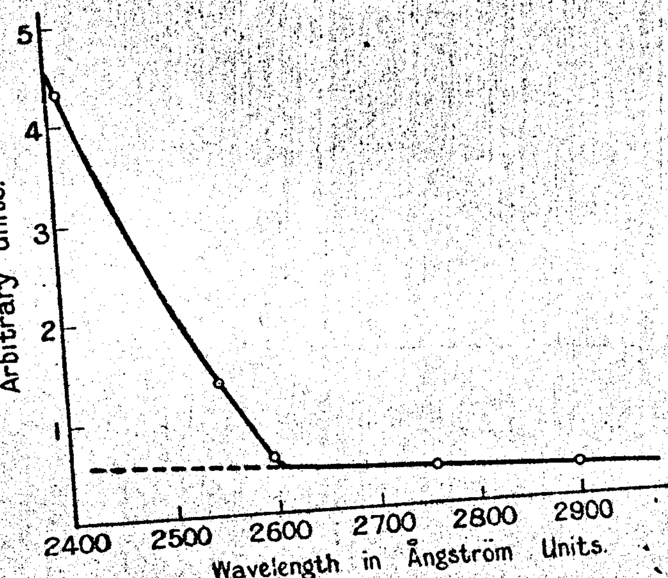
Significant evidence of the trustworthiness of these results is given by the more recent experiments at Yale. The curves of figs. 3 and 4 are representative of the later results, and are seen to be of the same form as previously obtained at Chicago (fig. 2). There were two changes in the Yale apparatus of importance—namely, the monochromator and the photoelectric cell. A Gaertner instrument was used with

Fig. 4.—"Yale Data."



Ordinates and abscissæ same as for fig. 3.
Currents measured by high-resistance method with electrodes at following potentials:—

Walls of ionization chamber	0·0 volts.
Grid	−11·0 „
Plate	− 9·9 „

slit-widths of 1 mm. (giving wave-length bands of forty to eighty ångströms), and a new photocell was built similar to the one used at Chicago. In view of these changes, it is interesting to note the agreement in the threshold values obtained, an agreement perhaps more complete than should be expected. Of interest also is the similarity of the curves to the right of the threshold, which suggests that either the two monochromators are quite equally defective in their function of producing monochromatic light, or that in all instances the amount of scattered light was about the same. This latter possibility suggests that the vapour was responsible for the scattering. The form of the results embodied in the above curves is a function of the selectivity of the photoelectric cell. This accounts for the more pronounced curvature of the Yale curves (figs. 3 and 4). Finally, the data indicate that the observed photoelectric effects in the vapour are practically independent of both the potentials on the electrodes in the ionization chamber and the condition of the vacuum. In all cases the photoelectric effects observed have been of the form exhibited above, although a range of potentials from eight to twenty-two volts has been used, and the vacuum, as indicated on a McLeod gauge, has ranged from 10^{-3} mm. to 10^{-5} mm.

Because of the difficulties in measuring light intensities in the ultra-violet, the calibration of the photocell lacked precision and was extended only to 2580 ångströms. It was found that the selectivity of the cell was qualitatively similar to that of new potassium metal surfaces as found by Souder *. On the basis of this calibration, the probable variation of the photoelectric effect in the vapour per unit intensity of light as a function of the wave-length is given by the curve of fig. 5. Although a slight curvature is exhibited—suggesting a maximum—it is entirely possible that more reliable intensity measurements will show that this is a linear relation. It is hoped that this point will be settled in the near future. For the present, it can be asserted that only light of wave-length shorter than 2610 Ångström units is able to produce a photoelectric effect in a stream of potassium vapour, and that the magnitude of the effect per unit light intensity is greater for shorter wave-lengths.

Williamson † has interpreted his results as indicating the photoelectric threshold at the Bohr theoretical value, namely 2856 ångströms. However, it is interesting to note that his published data are well in accord with the value herein given. It is interesting further to observe that the present results confirm his conclusion that light of shorter wave-lengths is more efficient in producing the photoelectric effect in the vapour jet, and that the general effects observed were independent of the electrode potentials,

* Phys. Rev. viii. p. 310 (1916).
† Phys. Rev. xxi. p. 107 (1923).

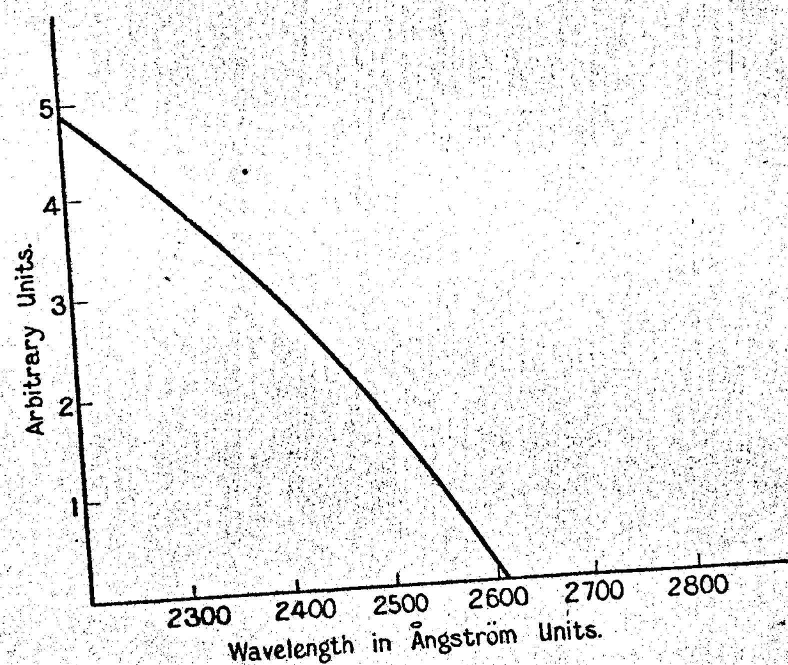
including potentials below the ionization potential of the vapour.

Discussion.

Researches on the absorption of light in alkali vapours reveal that wave-lengths of the principal series are absorbed as well as wave-lengths shorter than the series limit. The Bohr theory attributes the former phenomenon to the

Fig. 5.

Photoelectric effects in stream of potassium vapour per unit intensity of light.



Ordinates are photoelectric currents produced in vapour produced by light of wave-length given by abscissæ.

Photoelectric threshold at 2610 ångströms.

energy given up by the light in removing electrons from the 1s to the various *p* orbits, and the latter to a photoelectric effect. Light-quanta of greater frequency than the series limit have more than enough energy to eject an electron from the atom, and the surplus is used in giving the electron a velocity after ejection.

Corresponding phenomena occur in the X-ray region. There an absorption is observed which decreases approximately as the cube of the wave-length from the K, L, and M limits. In this instance also the absorbed energy goes into the jumps of the electrons from various orbits and their velocity upon complete removal from the atom. The velocities of these X-ray photoelectrons have been measured and found to agree with this view, and in general all the experimental evidence supports this photoelectric origin of the absorption.

Continuous optical absorption of wave-lengths shorter than the series limit has been obtained by Wood * in sodium and by Holtsmark † in sodium and potassium, and more recently Harrison ‡ has published excellent photometric measurements of the variation of the absorption with the wave-length. Harrison's results indicate that the absorption decreases with the wave-length from the series limit in a manner similar to the decrease beyond the absorption limits in the X-ray region. By analogy with the X-ray photoelectric data this similarity suggests that this continuous absorption is due to a photoelectric effect in the vapour, in agreement with the Bohr theory. However, as has been pointed out, direct photoelectric evidence is meagre, and the present research was initiated with the hope of obtaining more definite data of this sort.

Williamson has discussed in detail the experimental evidence from which is concluded that the effects observed are photoelectric effects in the vapour. In the present instance it is sufficient to say that his evidence and conclusions have been confirmed. Now, clearly, the results obtained are completely in disaccord with expectations. Neither does the photoelectric threshold coincide with the limiting wave-length of the principal series, nor is the light of wave-length just less than the threshold the most effective in producing the photoelectric effect. If these results are truely representative of the photoelectric effect from potassium atoms in the vapour, we have here an apparent serious difficulty for the Bohr theory.

The most plausible explanation of the difficulty is that the vapour consists of aggregates of potassium atoms, most probably in a sort of diatomic molecular form. Then, if an energy of ·4 volt is assigned to that involved in dissociation,

* Astrophys. Journ. xxix. 97 (1909).
† *Phys. Zeit.* xx. p. 88 (1919).
‡ Phys. Rev. xxiv. p. 466 (1924).

we have as the total energy required to ionize a molecule

$$\underset{\text{(Dissociation)}}{\cdot 4 \text{ volt}} + \underset{\text{(Ionization)}}{4{\cdot}3 \text{ volts}} = 4{\cdot}7 \text{ volts},$$

corresponding to the energy of a quantum of wave-length herein given as the threshold, viz. 2610 ångströms. That the vapour is in a molecular state receives support from other sources. Professor Wood * has observed channelled absorption bands in sodium vapour, and more recently H. D. Smith † has shown band absorption in potassium and other alkali vapours which strikingly suggests that a portion of the vapour is molecular. Clearly, if the number of such molecules is small relative to the number of atoms, the fact that the atomic photoelectric effect is not observed may be stated in another form, namely that the probability of a light-quantum ionizing a molecule is greater than that of its ionizing an atom.

Experiments are in progress designed to measure the initial velocities of the photoelectrons, and a method of positive-ray analysis is being developed to ascertain the nature of the photoelectric ions. Further theoretical speculation will be held in abeyance pending the outcome of this work.

Summary.

The photoelectric effect in a stream of potassium vapour has been observed, and it has been found that light of wave-length greater than 2610 ångströms produces no effect, and that the efficiency of the light in producing ionization increases as shorter wave-lengths are used. Because of the inconsistency with the Bohr theoretical interpretation of spectroscopic data on atomic potassium, the photoelectric effects observed are regarded as most probably due to a molecular state of the vapour.

The writer is very grateful to Professor W. F. G. Swann, who suggested the research, for his continued interest and many invaluable suggestions and criticisms throughout the course of the work, both at Chicago where the investigation was commenced and at Yale where it was completed.

Sloane Laboratory,
Yale University,
February 2, 1925.

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* Wood, 'Physical Optics,' 2nd edition.
† Smith, Proc. Roy. Soc. cvi. p. 400 (1924).